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(54) **MARTENSITE STAINLESS STEEL OF HIGH CORROSION RESISTANCE**

(57) A high-strength and high-toughness martensitic stainless steel, which is excellent in corrosion resistance to carbon dioxide, and which has no risk of cracking, even if used as welded under cathodic protection. The steel has the following basic composition (1) and satisfies the following condition (2).

(1) The composition containing, on a mass basis, C: not greater than 0.04%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, or further containing one or more of Si, Mn, Cu, S, Nb, Ti, Zr, Mo, W, Ca, Mg, and La in a specified amount.

(2) The following inequalities (1) and (2) are satisfied.

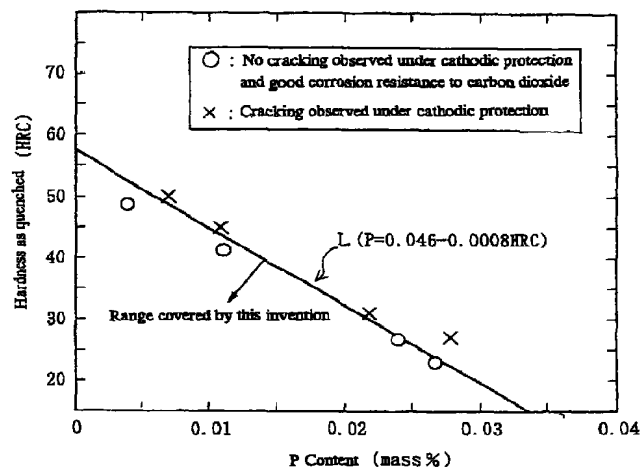
$$M=98+47C-1.1Cr+1.4Ni-150Al-200Nb-50Ti-200Zr-22(Mo+0.5W)\geq 50 \quad (1)$$

$$P\leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-1 to (1)-4 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

**EP 1 026 273 A1**

[FIG. 1]



## Description

### Technical Field

[0001] This invention relates to a high-corrosion-resistant martensitic stainless steel for use under cathodic protection. This stainless steel has excellent corrosion resistance in atmospheres, which contain carbon dioxide, and, therefore, it is suitable for use in line-pipes for transporting oil and natural gas, which contain carbon dioxide. Even if the pipe is used in a welded condition in the sea with cathodic protection, there is no risk that the pipe will suffer cracking.

[0002] The stainless steel of this invention is preferably used as a material for seamless pipes, resistance welded pipes, laser welded pipes, submerged arc welded (SAW) pipes and the like. In steel products other than pipes, such as plates, bars, and shape steels, this stainless steel may also be used as a material for various types of equipment exposed to atmospheres, which contain carbon dioxide. Such equipment includes, e.g., piping for decarbonating facilities, piping for geothermal power generation, and tanks for carbon dioxide-containing liquids. Furthermore, the stainless steel according to this invention can be used in environments, which contain a slight amount of hydrogen sulfide together with carbon dioxide.

### Background Art

[0003] Recently, the environments in wells for collecting oil or natural gas have become increasingly severe, and thus the corrosion of pipes for transporting these fluids has become a serious problem.

[0004] In order to prevent this corrosion problem, the following measures have conventionally been taken.

- (1) When carbon steels are used as piping materials, inhibitors for preventing corrosion are used.
- (2) Duplex stainless steels, having excellent corrosion resistance, are used as piping materials.

[0005] In either case, pipes to be laid down in the seawater are subjected to a cathodic protection process in order to protect the outer surfaces from corrosion.

[0006] In the method described in the first method (1) above, the pipes themselves are inexpensive, but the inhibitors are expensive and could cause environmental pollution. On the other hand, the duplex stainless steels in the second method (2) are expensive.

[0007] Many research papers are available on the corrosion resisting performance of a steel against carbon dioxide (hereinafter referred to as "corrosion resistance to carbon dioxide"). For example, it is reported by A. Ikeda et al., in Corrosion/83, NACE Houston. Paper No. 45, 1983, that a steel containing 7% or more Cr can be protected from carbon dioxide corrosion in an aqueous solution, which is as high as about 100°C and contains carbon dioxide. Further, M. Ueda et al. disclose in Corrosion/92, NACE Houston. Paper No. 55, 1992, that the localized corrosion resistance of a 13Cr martensitic stainless steel is improved by adding Mo and/or W.

[0008] On the basis of the above-described research results, attention has been paid recently to a 13Cr martensitic stainless steel, e.g., JIS SUS 410 steel, as a piping material which is resistant to carbon dioxide corrosion. A steel of this grade is used after subjected to a quenching-tampering heat treatment. When welded, the steel is subjected to a post weld heat treatment (hereinafter abbreviated as "PWHT"), for the purpose of assuring the toughness at welds and preventing delayed fracture (Kenji Satoh et al.: Corrosion/83, NACE Houston, Paper NO. 58, 1983).

[0009] Martensitic stainless steels are comparatively inexpensive, exhibit high strength and excellent corrosion resistance, and can be used without inhibitors. However, when used, e.g., as an undersea pipeline or the like in the seawater, the martensitic stainless steel needs to be subjected to cathodic protection for the prevention of corrosion to the outer surface, and when subjected to the cathodic protection, there arises a serious problem which is never encountered by carbon steels and duplex stainless steels.

[0010] Cathodic protection is a corrosion prevention method in which the corrosion current is cancelled by producing a protective current using a steel material to be corroded as the cathode. During this process, hydrogen is produced by the cathodic reaction, and the produced hydrogen is absorbed into the steel material. The welding heat affected zone of a 13Cr martensitic stainless steel has a quenched structure as welded, and exhibits an extreme hardness. When hydrogen is absorbed into such a zone, it suffers cracking due to hydrogen embrittlement.

[0011] It is thought that the cracking due to cathodic protection can be prevented to some degree by a heat treatment after welding (PWHT). However, for the conventional 13Cr martensitic stainless steel, the PWHT is not sufficient to reliably prevent the cracking caused by cathodic protection. In addition, it is comparatively easy to carry out the PWHT at a pipe making plant, but a PWHT, which is to be carried out after a peripheral welding at a site during the laying down of a pipeline, leads to a large increase in the operational costs.

[0012] From the above-described circumstances, there has been a strong demand for a martensitic stainless steel, free from the previously described cracking accompanied by cathodic protection. However, no martensitic stainless

steel intended to prevent the cracking at the welding heat affected zone, due to cathodic protection, has yet been proposed. U.S. Patent No. 5,383,983 (corresponding to Japanese Unexamined Patent Application Laid-Open No. 5-287455(1993)) discloses a martensitic stainless steel, which contains Ti or Zr as essential elements in the chemical composition and exhibits an excellent corrosion resistance. However, no consideration is given to that steel for the prevention of the cracking due to cathodic protection.

### Disclosure of the Invention

**[0013]** One of the objects of this invention is to provide a martensitic stainless steel having all of the following properties (a) to (d).

(a) To have an excellent corrosion resistance, particularly, in environments which contain carbon dioxide or a slight amount of hydrogen sulfide together with carbon dioxide.

(b) To have a proof stress (0.2% proof stress) of 550MPa (80ksi) or more when quenched and tempered.

(c) To have no risk of cracking due to cathodic protection, even if used as welded without a PWHT.

**[0014]** Another object of this invention is to provide a steel tube, which is made of a martensitic stainless steel, having the above-described properties as a material. This steel pipe includes seamless pipes, and welded pipes such as resistance welded pipes, laser welded pipes, and SAW pipes.

**[0015]** The basic chemical composition of the martensitic stainless steel according to this invention is as follows.

(1) A composition containing, on a mass basis, as essential elements: C: not greater than 0.04%, Cr: 7-15%, Ni: 0.7-8.0%, and Al: 0.001-0.20%.

(2) A composition consists essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2%, S: not greater than 0.01%, N: not greater than 0.05%, and a balance of Fe and incidental impurities.

(3) In addition to the elements in the composition of (2), a composition further contains one or more of alloying elements selected from at least one of the following first group elements, second group elements, and third group elements:

First group elements Nb: 0.005-0.10%, Ti: 0.005-0.10%, and Zr: 0.005-0.10%;

Second group elements Mo and W: 0.2-3.0% in terms of Mo+0.5W; and

Third group elements Ca: 0.001-0.05%, Mg: 0.001-0.05%, La: 0.001-0.05%, and Ce: 0.001-0.05%.

**[0016]** The martensitic stainless steel of this invention has the basic composition described in (2) or (3) above, and further satisfies any of the following inequalities (1)-1 to (1)-4, and the following inequality (2). In the case of the basic composition described in (2) above:

$$M=98+47C-1.1Cr+1.4Ni-150Al \geq 50 \quad (1)-1$$

In the case where only the first group elements are contained in the basic composition described in (3) above:

$$M=98+47C-1.1Cr+1.4Ni-150Al-200Nb-50Ti-200Zr \geq 50 \quad (1)-2$$

In the case where only the second group elements are contained in the basic composition described in (3) above:

$$M=98+47C-1.1Cr+1.4Ni-150Al-22(Mo+0.5W) \geq 50 \quad (1)-3$$

In the case where the first and second group elements are contained in the basic composition described in (3) above:

$$M=98+47C-1.1Cr+1.4Ni-150Al-200Nb-50Ti-200Zr-22(Mo+0.5W) \geq 50 \quad (1)-4$$

$$P \leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-1 to (1)-4, and the inequality (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched. Note that the inequalities (1)-1 to (1)-4 will be collectively referred to as "inequality (1)" in the following description.

## Brief Description of the Drawings

[0017]

- 5 FIG. 1 is a diagram showing a relationship among the P (phosphorus) content, hardness as quenched, and corrosion resistance of a martensitic stainless steel;  
 FIG. 2 is a table showing the chemical compositions of test materials used in examples;  
 FIG. 3 is another table showing the chemical compositions of test materials used in examples;  
 FIG. 4 is a table showing the test results of the examples; and  
 10 FIG. 5 is another table showing the test results of the examples.

## Best Mode for Carrying out the Invention

15 [0018] A stainless steel of this invention has the properties described previously in (a) to (c), as a combined effect of the previously described basic compositions, and the conditions specified by the inequalities (1) and (2). Among those, the most significant characteristic feature is that the steel of this invention has no risk of cracking, even if subjected to cathodic protection, as welded. Thus, this feature will be described first.

[0019] A welding heat affected zone is heated through a weld heat input, and is thereafter rapidly cooled by the chill effect of the base metal. Its heat pattern is substantially the same as that for quenching. Therefore, the inventors  
 20 thought, on the assumption that the steel would be used as welded, that the phenomena of corrosion and cracking due to cathodic protection observed at the welding heat affected zone could be evaluated in terms of the phenomena observed in a steel as quenched. Hence, specimens of a 13Cr martensitic stainless steel as quenched were prepared and their metallographic structure, corrosion resistance to carbon dioxide, and a tendency toward cracking due to  
 25 cathodic protection, were investigated. As a result, it was clarified that in order to prevent carbon dioxide corrosion and cracking due to cathodic protection, the following conditions 1 and 2 need to be satisfied at the same time.

1. The rate of martensite of a metallographic structure as quenched needs to be 95% or more.
2. A relationship between the content of P (phosphorus) and hardness (HRC) as quenched of a steel needs to satisfy  $P \leq 0.046 - 0.0008\text{HRC}$  (the previously described inequality (2)).

30

[0020] The fact that the rate of martensite is less than 95% means that the steel has a structure other than martensite, e.g., austenite or ferrite mixed in a large amount, and in this case, cracking tends to occur under cathodic protection. This is due to corrosion being promoted at regions other than the martensitic structure, and thus hydrogen is produced by the corrosion reaction, which in turn increases the amount of hydrogen absorbed into the steel.

35 [0021] A structure which is quenched at a rate of martensite of 95% or more can be obtained by adjusting the chemical composition of the steel. A specific condition for the adjustment of the chemical composition is the previously described inequality (1). That inequality is an empirical formula obtained from the results of a number of tests conducted by the inventors.

[0022] FIG. 1 is a diagram showing the results of carbon dioxide corrosion tests and cracking tests under cathodic protection, which will later be described in "Example". The base steel consists of C: 0.01-0.039%, Si: 0.31-0.36%, Mn: 1.09-2.60%, S: 0.003-0.005%, Cr: 11.7-12.2%, Ni: 1.8-2.1%, Al: 0.08-0.11%, and the balance of Fe. Test specimens were prepared from the base steel by varying the P content and the hardness as quenched in varying degrees. Note that the test specimens were obtained by adjusting the chemical compositions so as to become structures whose rate of martensite is 95% or more as quenched (so as to satisfy the previously described inequality (1)), with their hardness  
 45 varied by adjusting the contents of C and Mn.

[0023] The lower part demarcated by the straight line L in FIG. 1 is a region where the steels exhibit excellent corrosion resistance to carbon dioxide and suffer no cracking under cathodic protection. Since the straight line L is expressed as  $P = 0.046 - 0.0008\text{HRC}$ , the above-described desired region can be expressed as  $P \leq 0.046 - 0.0008\text{HRC}$  (inequality (2)). What is meant by this inequality (2) is that the hardness of a steel as quenched can be comparatively  
 50 high if the P content is low, while the hardness of a steel as quenched needs to be low if the P content is comparatively high.

[0024] The reasons why the basic composition of the steel according to this invention has been determined as above will be described below. Note that the unit "%" herein means "% by mass" unless otherwise specified.

55 C:

[0025] When the content of C exceeds 0.04%, the hardness of a steel as quenched, whose rate of martensite is 95% or more, becomes too high to suffer cracking under cathodic protection. The lower the C content, the better. There-

fore, the C content is set at 0.04% or less. The lower the C content is, the more satisfactory the toughness of the heat affected zone of the steel as welded becomes, therefore, the desirable upper limit of the C content is 0.025%, and the more desirable upper limit is 0.015%. Note that the lower limit is on the order of 0.001% from the viewpoint of manufacturing the steel economically.

Si:

[0026] Silicon is an element necessary to deoxidize steels. When its content exceeds 1.0%, hot workability is degraded. Therefore, its upper limit is set at 1.0%. No deoxidizing effect can be obtained when the Si content is less than 0.01%.

Mn:

[0027] Manganese is also an element necessary as a deoxidizer for steels. When its content exceeds 1.5%, hot workability is degraded, therefore, its upper limit is set at 1.5%. No deoxidizing effect can be obtained when the Mn content is less than 0.1%.

Cr:

[0028] Chromium is an element for improving corrosion resistance to carbon dioxide and no sufficient corrosion resistance to carbon dioxide can be obtained when the Cr content is less than 7%. On the other hand, when the Cr content exceeds 15%, it is difficult to obtain a rate of martensite of 95% or more for steels as quenched, therefore, the Cr content is set between 7 and 15%. Preferably, it is between 9 and 13%.

Ni:

[0029] In order to obtain a rate of martensite of 95% or more as quenched, the Ni content of a steel needs to be in the range of 0.7-8.0%, because when the Ni content is less than 0.7%, the formation of ferrite is promoted and when it exceeds 8.0%, the amount of austenite is increased. The preferable Ni content is in the range of 0.7-7.0%. Note that excellent properties can be obtained even if the Ni content is within such a low range of 0.7 to less than 4.0%, and thus a possible reduction in the material costs is one of the characteristic features of the steel according to this invention.

Al:

[0030] Similarly to Si, Al is a necessary element as a deoxidizer in the steel making process. When its content is less than 0.001%, no desired deoxidizing effect can be obtained. On the contrary, when its content exceeds 0.20%, nonmetallic inclusions increase and thus the corrosion resistance is degraded. Hence, the Al content was set between 0.001 and 0.20%.

Cu:

[0031] Although not an essential element, Cu has the effect of suppressing the corrosion of steels and reducing the production of hydrogen to thereby prevent cracking under cathodic protection, and thus Cu can be added whenever necessary. However, when its content exceeds 2%, its effect gets saturated. Therefore, even if Cu is added, it is desirable that its content is up to 2%.

N:

[0032] When the content of N exceeds 0.05%, the hardness of the welding heat affected zone of a steel as quenched, becomes so high that the steel is susceptible to cracking under cathodic protection. Therefore, the N content should be kept at 0.05% or lower.

P:

[0033] One of the significant characteristic features of this invention is that the content of P is regulated in relation to the hardness (HRC) of an as-quenched steel. The reasons for such regulation have already been described.

[0034] Note that a P content in excess of 0.03% causes the action of promoting sulfide corrosion cracking to appear in hydrogen sulfide environments and thus it is desirable to adjust the chemical composition of a steel, so as to satisfy

the previously described inequality (2) with the tolerable upper limit of P set at 0.03%.

S:

- 5 [0035] Sulfur is also present as an impurity in steels. Since S impairs hot workability when its content exceeds 0.01%, its upper limit is set at 0.01%. The less, the better. However, the lower limit, permitting economical manufacture, is on the order of 0.0007%.

First Group Elements (Nb, Ti, Zr):

10

[0036] One or more of Nb, Ti and Zr are added whenever necessary in order to fix C and reduce fluctuations in strength. Content of each of these elements, in an amount of less than 0.005%, is not effective. Content of each in an amount exceeding 0.10% cannot achieve a rate of martensite of 95% or more, and the hardness of a steel as quenched also becomes so high that the risk of cracking, due to cathodic protection, is increased. Note that these elements may be added singly or in combination of two or more.

15

[0037] Since the first group elements are not essential, none of them need be added at all. However, some addition of them in slight amounts, provides the effect of fixing C, so it is desirable to add them, considering the economy, in the range of less than 5 x C (%) Nb, less than 4 x C(%)Ti, and less than 10 x C(%)Zr.

20 Second Group Elements (Mo, W):

[0038] Molybdenum and tungsten are elements that prevent localized corrosion in carbon dioxide environments, while present with Cr, therefore, for steels used in particularly severe corrosive environments, it is desirable that the steel contains one or both Mo and W in amounts ranging from 0.2 to 3.0% in terms of "Mo+0.5W." No sufficient improvement of localized corrosion resistance is observed with their contents being less than 0.2%, while there is little increase in their effect when the amounts exceed 0.3%.

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Third Group Elements (Ca, Mg, La, Ce):

- 30 [0039] All of Ca, Mg, La and Ce are effective in improving the hot workability of steels. Therefore, to obtain this effect, one, or two or more of them may be selected and added. However, the above-described effect cannot be obtained when content of any of these elements is less than 0.001%. On the other hand, a content exceeding 0.05% produces coarse oxides, which reduce the corrosion resistance of steels, therefore, when these elements are added, each of the contents should be between 0.001 and 0.05%. Note that Ca and La are particularly preferable among these elements.

35

[0040] The martensitic stainless steel of this invention is used after subjected it to a quenching-tempering heat treatment. This heat treatment may be carried out under ordinary conditions; for example, a water quenching process from the temperature of Ar<sub>3</sub> point or higher and a subsequent tempering process at 600-670°C, for 5-60 minutes, may be performed. Through such heat treatment, the steel of this invention is given a proof stress of 550MPa or more and an excellent toughness.

40

[0041] When welded, the heat affected zone that comes in contact with the weld metal is brought to a quenched state, and thus it has an extreme hardness. Even in this state, the heat affected zone of the steel, according to this invention, is satisfactory in toughness and corrosion resistance with its rate of martensite being 95% or more, and also has no risk of cracking under cathodic protection. Note that it is, of course, further desirable to subject the steel to a heat treatment (PWHT) for the purpose of softening the heat affected zone, after welding.

45

[0042] Next, the effects of this invention will be described more specifically by way of examples.

### Examples

- 50 [0043] Steels whose chemical compositions are as shown in FIGS. 2 and 3 were prepared by melting with an ordinary electric furnace and by refining with an argon-oxygen decarburizing furnace (AOD furnace) for desulfurization. The steels were cast into 500-mm-diameter ingots, and billets having 150 mm in diameter were obtained by hot forging the ingots at 1200°C. Seamless steel pipes, having 168 mm in outside diameter and 12 mm in thickness, were manufactured by the Mannesmann pipe making process.

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[0044] The following test materials were prepared from the above described seamless steel pipes.

(a) Pipes quenched by air cooling or water cooling, after heated for 30 minutes, at 950°C.

(b) Pipes subjected to tempering in which the pipes described in (a) above were heated for 30 minutes at 600°C

and thereafter air-cooled.

(c) Welded pipes obtained by peripherally welding the pipes described in (b) above.

[0045] The welding of the pipes of (c) was effected in accordance with ASTM 1G by a gas-tungsten arc welding method (GTAW) or a shield metal arc welding method (SMAW), using a welding material made of a 25Cr duplex stainless steel.

[0046] The following tests were conducted using the test materials described in (a) to (c) above.

(A) Measurement of Hardness

[0047] Cross-sections perpendicular to their longitudinal direction were cut out of the as-quenched pipes, previously described in (a), and their HRC hardnesses were measured.

(B) Rate of Martensite

[0048] Cross-sections perpendicular to their longitudinal direction were cut out of the as-quenched pipes previously described in (a), and ten views of their microstructure were observed for each of the cross-sections, at a magnification of 100, using an optical microscope to thereby measure the rates of martensite (area rates) and obtain the average.

(C) Tensile Test

[0049] Test specimens having 4.0-mm-diameter and 20-mm-long parallel portion were obtained from the quenched-tempered material previously described in (b). These test specimens were subjected to a tensile test, at ambient temperature, to obtain 0.2% proof stresses.

(D) Charpy Test

[0050] Full-size Charpy test specimens (10 mm x 10 mm x 55 mm, 2 mm V-notch) were cut out of the welding heat affected zones of the as-welded pipes previously described in (c), and were tested at varying temperatures, to obtain the temperatures at which their rate of brittle fracture surface becomes 50%.

(E) Carbon Dioxide Corrosion Test

[0051] Test specimens measured 22 mm (w) x 3 mm (t) x 76 mm (l), which were cut out of the as-welded test material previously described in (c), polished with an emery paper No.600, and thereafter degreased and dried, were used. The test specimens were cut out of locations including the welding heat affected zone and the weld metal.

[0052] The above-described test specimens were immersed for 720 hours in a 5%NaCl aqueous solution (the temperature of the solution was 125°C and the flow velocity was 3.5 m/s) in which CO<sub>2</sub> was saturated at a pressure of 30 atm.

[0053] Then, if the test specimens suffered localized corrosion or not was visibly observed, and a mass loss (the value obtained by subtracting the weight of each test specimen after the test from the weight of each test specimen before the test) of each test specimen was measured, and the mass loss was converted into a corrosion rate (mm/year).

(F) Cracking Test under Cathodic Protection

[0054] Using test specimens cut out of locations including the welding heat affected zone and the weld metal of the as-welded test material previously described in (c), tests were conducted under the following conditions.

Testing solution:	Artificial seawater
Potential:	-1300 mV vs.SCE
Testing temperature:	25°C
Immersion time:	720 hours
Applied stress:	100% of the 0.2% proof stress of the base metal
Test specimens:	10 mm (w) x 2mm (t) x 75 mm (l) (for four-point bending test)

[0055] The results of the above tests are shown in FIGS. 4 and 5. In these drawings, the marks "O" and "x" indicated in the columns have the following meanings.

[0056] In the column for toughness;



- O: Temperature, wherein the rate of brittle fracture surface is 50%, is -30°C or lower.  
 x: Temperature, wherein the rate of brittle fracture surface is 50%, is higher than -30°C.

**[0057]** In the column for corrosion resistance to carbon dioxide

- O: Corrosion rate is 0.05 mm/year or less and no localized corrosion observed.  
 x: Corrosion rate exceeds 0.05 mm/year and localized corrosion observed, or localized corrosion observed even if corrosion rate is 0.05 mm/year or less.

**[0058]** In the column for cracking under cathodic protection

- O: No cracking observed  
 x: Cracking observed

**[0059]** The test Nos. 1 to 44 shown in FIGS. 2 and 3 are stainless steels according to this invention. The rates of martensite of these steels as-quenched and their values M calculated from the previously described inequality (1) are shown in FIGS. 4 and 5. Further, the allowable upper limits of hardness (HRC) calculated from the previously described inequality (2), i.e., the values of  $(0.046-P)/0.0008$  are also presented in these drawings.

**[0060]** It is apparent from the test results shown in FIGS. 4 and 5, that all the steels exhibited a rate of martensite of 95% or more as quenched, and their 0.2% proof stresses, after subjected to the quenching-tempering treatment, are 550MPa or more. These steels do not suffer cracking under cathodic protection even as welded, and were also excellent in corrosion resistance to carbon dioxide.

**[0061]** The above-described excellent properties are provided by the combined effect of the basic chemical composition being appropriate, the rate of martensite of 95% or more as quenched being achieved by satisfying the previously described inequality (1), and the relationship between the P content and hardness (HRC) satisfying the previously described inequality (2).

**[0062]** Test Nos. 45 to 62 steels of FIG. 3 were prepared as comparative examples. In these steels, Nos. 53 to 55 steels and Nos. 60 to 62 steels, whose chemical compositions are outside the range specified by this invention are, as shown in FIG. 5, inferior in part or in whole in their properties as welded.

**[0063]** Test Nos. 45, 48 to 52 and 56 to 59 steels do not satisfy the condition specified by the previously described inequality (2). That is, their hardnesses after quenching exceed the allowable upper limits calculated from the inequality (2). These steels suffer cracking under cathodic protection. Test Nos. 46 and 47 steels have their M values less than 50 and these steels have low rates of martensite after quenching, and thus poor in toughness, and suffer cracking under cathodic protection.

## Industrial Applicability

**[0064]** The martensitic stainless steel of this invention is a high-strength, high-toughness steel, excellent in corrosion resistance to carbon dioxide, and has no risk of cracking even if used as welded under cathodic protection. This steel is extremely suitable for use as linepipe for transporting crude oil and the like, which contain carbon dioxide, particularly, while subjected to cathodic protection in the sea. Since this steel requires no heat treatment after welded, it can exhibit the economy of a martensitic stainless steel at a satisfactory level, and thus has a significant practical advantage.

## Claims

1. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by containing, on a mass basis, C: not greater than 0.04%, Cr: 7-15%, Ni: 0.7-8.0%, and Al: 0.001-0.20%, and by satisfying the following inequalities (1)-1 and (2):

$$M=98+47C-1.1Cr+1.4Ni-150Al \geq 50 \quad (1)-1$$

$$P \leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-1 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

2. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by

# EP 1 026 273 A1

consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, the balance of Fe and incidental impurities, and further characterized by satisfying the following inequalities (1)-1 and (2):

$$M=98+47C-1.1Cr+1.4Ni-150Al\geq 50 \quad (1)-1$$

$$P\leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-1 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

3. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, one or more of the following first group elements, the balance of Fe and incidental impurities, and further characterized by satisfying the following inequalities (1)-1 and (2):

First group elements Nb: 0.005-0.10%, Ti: 0.005-0.10%, and Zr: 0.005-0.10%

$$M=98+47C-1.1Cr+1.4Ni-150Al-200Nb-50Ti-200Zr\geq 50 \quad (1)-2$$

$$P\leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-2 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

4. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, one or more of the following second group elements, the balance of Fe and incidental impurities, and further characterized by satisfying the following inequalities (1)-3 and (2):

Second group elements Mo and W: 0.2-3.0% in terms of Mo+0.5W

$$M=98+47C-1.1Cr+1.4Ni-150Al-22(Mo+0.5W)\geq 50 \quad (1)-3$$

$$P\leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-3 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

5. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, one or more of the following third group elements, the balance of Fe and incidental impurities, and further characterized by satisfying the following inequalities (1)-1 and (2):

Third group elements Ca: 0.001-0.05%, Mg: 0.001-0.05%, La: 0.001-0.05%, and Ce: 0.001-0.05%

$$M=98+47C-1.1Cr+1.4Ni-150Al\geq 50 \quad (1)-1$$

$$P\leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-1 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

6. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni:

# EP 1 026 273 A1

0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, one or more of the following first group elements, one or more of the following second group elements, the balance of Fe and incidental impurities, and further characterized by satisfying the following inequalities (1)-4 and (2):

5 First group elements Nb: 0.005-0.10%, Ti: 0.005-0.10%, and Zr: 0.005-0.10%  
Second group elements Mo and W: 0.2-3.0% in terms of Mo+0.5W

$$M=98+47C-1.1Cr+1.4Ni-150Al-200Nb-50Ti-200Zr-22(Mo+0.5W)\geq 50 \quad (1)-4$$

$$10 \quad P\leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-4 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

15 7. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, one or more of the following first group elements, one or more of the following third group elements, the balance of Fe and incidental impurities, and further by satisfying the following inequalities (1)-1 and (2):

20 First group elements Nb: 0.005-0.10%, Ti: 0.005-0.10%, and Zr: 0.005-0.10%  
Third group elements Ca: 0.001-0.05%, Mg: 0.001-0.05%, La: 0.001-0.05%, and Ce: 0.001-0.05%

$$M=98+47C-1.1Cr+1.4Ni-150Al\geq 50 \quad (1)-1$$

$$25 \quad P\leq 0.046-0.0008HRC \quad (2)$$

where the symbols of the elements in the inequalities (1)-2 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

30 8. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, one of more of the following second group elements, one or more of the following third group elements, the balance of Fe and incidental impurities, and further characterized by satisfying the following inequalities (1)-3 and (2):

35 Second group elements Mo and W: 0.2-3.0% in terms of Mo+0.5W  
Third group elements Ca: 0.001-0.05%, Mg: 0.001-0.05%, La: 0.001-0.05%, and Ce: 0.001-0.05%

$$40 \quad M=98+47C-1.1Cr+1.4Ni-150Al-22(Mo+0.5W)\geq 50 \quad (1)-3$$

$$P\leq 0.046-0.0008HRC \quad (2)$$

45 where the symbols of the elements in the inequalities (1)-3 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

50 9. A high-corrosion-resistant martensitic stainless steel, which is used under cathodic protection, characterized by consisting essentially, on a mass basis, of: C: not greater than 0.04%, Si: 0.01-1.0%, Mn: 0.1-1.5%, Cr: 7-15%, Ni: 0.7-8.0%, Al: 0.001-0.20%, Cu: 0-2, S: not greater than 0.01%, N: not greater than 0.05%, one or more of the following first group elements, one or more of the following second group elements, one or more of the following third group elements, the balance of Fe and incidental impurities, and further characterized by satisfying the following inequalities (1)-4 and (2):

55 First group elements Nb: 0.005-0.10%, Ti: 0.005-0.10%, and Zr: 0.005-0.10%  
Second group elements Mo and W: 0.2-3.0% in terms of Mo+0.5W  
Third group elements Ca: 0.001-0.05%, Mg: 0.001-0.05%, La: 0.001-0.05%, and Ce: 0.001-0.05%

$$M=98+47C-1.1Cr+1.4Ni-150Al-200Nb-50Ti-200Zr-22(Mo+0.5W)\geq 50 \quad (1)-4$$

where the symbols of the elements in the inequalities (1)-4 and (2) indicate the contents (% by mass) of the respective elements, and HRC in the inequality (2) indicates the Rockwell C-scale hardness of the steel as quenched.

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**10.** A martensitic stainless steel according to any of claims 1 to 9, wherein the content of Ni is less than 4.0% by mass.

**11.** A steel pipe for use in seawater while subjected to cathodic protection, which is made of a steel according to any of claims 1 to 10.

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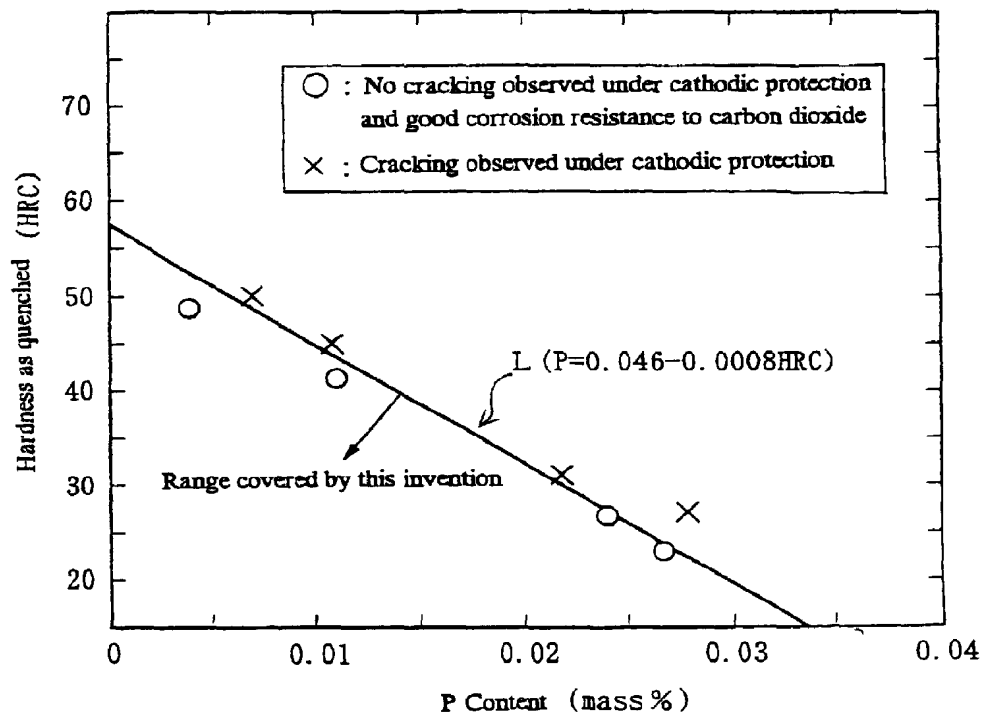
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[FIG. 1]



[FIG. 2]

Test No.	O	Si	Mn	P	S	Cr	Ni	Al	Mo	W	Mg <sup>+</sup> 0.5W	Nb	Ti	Zr	N	Others
1	0.006	0.36	0.55	0.013	0.005	11.2	3.5	0.10	0.5		0.5		0.03		0.008	
2	0.008	0.11	0.15	0.012	0.001	7.1	1.1	0.07					0.02	0.02	0.008	
3	0.005	0.17	0.25	0.009	0.001	9.2	2.0	0.15							0.010	
4	0.014	0.25	0.2	0.010	0.001	10.5	3.0	0.05					0.01		0.010	
5	0.003	0.47	0.48	0.016	0.001	13.5	5.8	0.11					0.02		0.020	
6	0.011	0.58	0.76	0.018	0.002	11.5	5.2	0.08	1.0		1		0.05	0.01	0.020	
7	0.010	0.81	1.4	0.010	0.003	10.3	4.1	0.07		1.0	0.5		0.06		0.010	0.0008
8	0.009	0.05	0.33	0.025	0.002	12.7	5.5	0.05	1.0	1.0	1.5		0.03		0.020	Mg:0.007
9	0.005	0.28	0.67	0.011	0.001	11.5	5.0	0.12					0.02		0.010	0.0001
10	0.008	0.55	0.47	0.008	0.001	7.5	1.5	0.03					0.03		0.008	0.0001, 1.0e-005
11	0.011	0.34	1.11	0.015	0.005	12.0	2.0	0.10					0.02		0.013	
12	0.010	0.34	1.08	0.015	0.005	12.2	2.0	0.10					0.02		0.013	
13	0.015	0.24	1.08	0.015	0.003	12.3	1.8	0.09					0.03		0.014	
14	0.025	0.34	1.09	0.015	0.003	12.6	1.9	0.08					0.03		0.022	
15	0.023	0.35	1.11	0.015	0.003	12.9	1.5	0.08					0.05		0.013	
16	0.013	0.35	1.11	0.015	0.003	12.3	1.9	0.09					0.03		0.011	
17	0.010	0.31	1.10	0.027	0.004	11.8	1.8	0.09					0.02		0.008	
18	0.012	0.33	1.09	0.024	0.003	11.7	1.8	0.08					0.02		0.008	
19	0.028	0.31	1.87	0.011	0.005	12.1	2.1	0.10					0.02		0.010	
20	0.039	0.31	1.89	0.004	0.004	11.9	1.8	0.11					0.03		0.010	
21	0.005	0.08	1.11	0.016	0.008	7.2	6.7	0.15					0.01		0.010	
22	0.005	0.24	1.07	0.012	0.008	10.1	6.7	0.15					0.01		0.012	
23	0.014	0.34	1.08	0.012	0.005	14.1	2.1	0.05					0.03		0.012	
24	0.005	0.45	1.09	0.011	0.006	7.5	5.8	0.15					0.01	0.02	0.013	
25	0.007	0.83	1.10	0.009	0.008	9.5	5.5	0.13					0.01		0.013	
26	0.019	0.56	0.19	0.015	0.002	12.4	0.9	0.05					0.07		0.027	
27	0.020	0.70	0.19	0.014	0.002	12.4	1.0	0.04					0.07		0.027	
28	0.022	0.91	0.15	0.014	0.002	12.5	0.7	0.10					0.09		0.032	
29	0.024	0.34	0.13	0.015	0.002	12.7	0.7	0.11					0.09		0.027	
30	0.010	0.34	1.15	0.005	0.009	12.1	2.1	0.17					0.03		0.013	
31	0.009	0.36	1.19	0.007	0.008	11.8	2.1	0.17					0.03		0.008	
32	0.009	0.65	1.21	0.011	0.008	11.5	2.0	0.04	1.00		1.00		0.03		0.009	

Steels according to this invention

Test No.	Chemical Composition (mass%, Fe bal.)															
	C	Si	Mn	P	S	Cr	Ni	Al	Mo	W	Mo+ 0.5W	Nb	Ti	Zr	N	Others
Steels according to this invention	33	0.020	0.71	1.34	0.015	0.008	8.0	7.0	0.04	1.95		1.95		0.02	0.014	Cu:0.2
	34	0.008	0.71	1.34	0.015	0.007	12.7	2.2	0.04		0.5	0.25		0.02	0.08	0.013
	35	0.011	0.24	1.11	0.013	0.007	12.5	4.9	0.07		2.7	1.35		0.02		0.012
	36	0.010	0.24	1.08	0.018	0.005	12.5	1.5	0.07	0.10	0.5	0.35		0.05		0.012
	37	0.038	0.24	1.05	0.012	0.005	7.5	7.9	0.02	1.85	0.6	2.10		0.05		0.033
	38	0.010	0.91	1.38	0.011	0.003	10.3	4.1	0.05		1	0.50		0.04		Ce:0.005
	39	0.009	0.45	0.26	0.011	0.003	11.5	5.7	0.05	1.00		1.00		0.05		Ca:0.01
	40	0.009	0.05	0.33	0.020	0.003	12.7	5.5	0.03	1.00	1	1.50		0.03		Mg:0.007
	41	0.005	0.29	0.87	0.011	0.001	12.5	4.8	0.12					0.02		La:0.005
	42	0.010	0.83	0.58	0.015	0.002	7.2	7.9	0.01	2.10		2.10		0.05		Ca:0.01, La:0.005
	43	0.011	0.29	1.08	0.012	0.005	11.9	2.0	0.10				0.010			0.022
	44	0.013	0.25	1.11	0.015	0.003	12.3	2.2	0.08				0.051			Cu:0.4
	45	0.017	0.28	0.50	0.029	0.001	11.7	5.5	0.11					0.03		0.021
	46	0.013	0.79	0.25	0.017	0.002	12.8	5.0	0.02	1.5		1.5			0.05	0.022
Comparative steels	47	0.008	0.20	0.37	0.021	0.001	9.5	3.5	0.25	0.5	0.5	0.75		0.07		0.018
	48	0.021	0.35	1.11	0.015	0.005	12.3	2.0	0.10					0.01		0.034
	49	0.023	0.35	1.11	0.015	0.004	12.1	2.1	0.10					0.01		0.034
	50	0.019	0.33	1.08	0.015	0.004	11.9	2.1	0.09					0.01		0.028
	51	0.025	0.34	1.07	0.015	0.008	12.3	1.9	0.09					0.03		0.028
	52	0.021	0.34	1.08	0.015	0.003	12.3	1.9	0.12					0.03		0.028
	53	0.007	0.35	0.94	0.015	0.004	12.8	0.1	0.12	1.20		1.20		0.07		0.017
	54	0.005	0.35	0.94	0.015	0.004	12.5	0.2	0.09	0.84		0.84		0.07		0.012
	55	0.008	0.33	0.87	0.015	0.004	12.7	0.5	0.11	0.99		0.99		0.03		0.012
	56	0.013	0.33	1.50	0.028	0.005	12.2	1.9	0.11					0.02		0.011
	57	0.015	0.35	1.61	0.022	0.004	11.8	1.8	0.10					0.03		0.012
	58	0.029	0.35	2.40	0.011	0.003	11.7	1.8	0.09					0.02		0.008
	59	0.038	0.33	2.60	0.007	0.003	12.2	2.1	0.09					0.02		0.009
	60	0.043	0.24	2.65	0.018	0.001	12.5	1.9	0.04					0.07		0.013
	61	0.012	0.25	1.01	0.013	0.002	8.5	2.0	0.08				0.010	0.01		0.013
	62	0.003	0.25	1.01	0.011	0.002	15.2	0.8	0.19				0.051	0.09		0.011

[FIG. 3]

[illegible]



[FIG.5]

	Test No.	M	Upper Limit of Hardness Calculated from Inequality (2) (HRC)	Properties as Quenched		Proof Stress after Quenched (MPa)	Properties as Welded		
				Hardness (HRC)	Rate of Martensite (%)		Toughness	Corrosion Resistance to Carbon Dioxide	Cracking under Cathodic Protection
Steels according to This Invention	33	50.3	39	27	98	897	○	○	○
	34	59.0	39	23	96	601	○	○	○
	35	50.4	41	23	97	613	○	○	○
	36	66.1	38	24	97	598	○	○	○
	37	50.9	43	31	99	928	○	○	○
	38	72.4	44	28	98	583	○	○	○
	39	61.8	44	25	97	550	○	○	○
	40	58.2	33	23	99	613	○	○	○
	41	72.2	44	22	98	566	○	○	○
	42	51.4	39	26	98	575	○	○	○
	43	71.2	43	27	97	822	○	○	○
	44	64.5	39	29	98	915	○	○	○
Comparative Steels	45	75.6	21	28	98	630	○	○	×
	46	45.5	36	27	92	590	×	○	×
	47	35.3	31	22	85	595	×	×	×
	48	72.8	39	40	99	584	×	○	×
	49	73.2	39	42	96	588	×	○	×
	50	74.7	39	40	93	595	○	×	×
	51	73.3	39	42	92	595	○	×	×
	52	68.6	39	40	93	595	○	×	×
	53	36.7	39	31	85	623	×	×	×
	54	49.3	39	28	94	605	×	×	×
	55	45.3	39	26	92	595	×	×	×
	56	70.4	23	27	96	556	×	○	×
	57	71.7	30	31	96	561	○	○	×
	58	74.5	44	45	98	621	○	○	×
	59	74.8	49	50	98	648	○	○	×
	60	79.4	38	52	98	611	○	○	×
	61	81.7	41	23	99	585	○	○	×
	62	49.5	44	22	93	582	×	×	×

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/03243

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl <sup>6</sup> C22C38/00, 38/40, 38/42, 38/50  According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl <sup>6</sup> C22C38/00-38/60, C23F13/00  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 4-268019, A (Nippon Steel Corp.), 24 September, 1992 (24. 09. 92) (Family: none)	1-11
A	JP, 6-299301, A (NKK Corp.), 25 October, 1994 (25. 10. 94) (Family: none)	1-11
A	JP, 8-41599, A (Sumitomo Metal Industries, Ltd.), 13 February, 1996 (13. 02. 96) (Family: none)	1-11
A	JP, 8-199236, A (Nippon Steel Corp.), 6 August, 1996 (06. 08. 96) (Family: none)	1-11
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 October, 1998 (13. 10. 98)		Date of mailing of the international search report 27 October, 1998 (27. 10. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)